ASSESSMENT OF CO_2 EMISSIONS DURING ACIDIFICATION, STORAGE, AND AFTER INCORPORATION TO SOIL OF PIG SLURRY

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1 INTRODUCTION

Large amounts of pig slurry are produced each year in Portugal leading to environmental problems such as water and air pollution. Previous studies have reported that livestock production is the main source of anthropogenic ammonia (NH_3) emissions in Europe (Kai et al., 2008) and an important source of greenhouse gases (Weiske and Petersen, 2006). Effluent treatment has been promoted to improve slurry management and to reduce its environmental impact (Sommer and Hutchings, 2001, Fangueiro et al., 2008a). Solid-liquid separation of slurry is a useful tool at the farm level producing valuable fractions, a liquid that can be used for direct fertilisation and a solid fraction that can be composted (Fangueiro et al., 2008b). Alternatively, acidification of slurry has been proposed to reduce ammonia (NH_3) emissions during storage and field application (Kai et al., 2008). Previous works (Misselbrook et al., 2005; Fangueiro et al., 2008a) reported that higher NH_3 emissions occurred during storage of liquid fraction of slurry or manure with low dry matter content, probably due to a reduced crust formation that decreases NH_3 emissions. Hence, acidification of the liquid fraction of slurry is strongly recommended. Slurry acidification is common practice in The Netherlands and Denmark (Schils et al., 1999; Eriksen et al., 2008) but this technology still needs to be improved to avoid hazards. It is expected that this technology will be used in more countries since the European Directive (2001/81/CE) demands a decrease of atmospheric pollutants such as NH_3: targets for lower NH_3 emissions have been already set in Spain (Castrillon et al., 2009). Nevertheless, the acidification process leads to significant carbon dioxide (CO_2) emissions (Vandré and Clemens, 1997). Such CO_2 release is problematic when a closed system of slurry acidification is used (when acidified slurry is flushed back to pig houses) since it may lead to foam formation (Vandré and Clemens, 1997; Borst, 2001). Nevertheless, Fangueiro et al. (2010) reported that acidification of slurry or derived fractions led to a decrease in CO_2 emissions following soil addition relative to non acidified materials.

The aim of the present work was to measure the CO_2 emissions during the acidification process of the liquid fraction of pig slurry and its subsequent impact during storage and after soil incorporation.

2 MATERIALS AND METHODS

2.1 CO_2 emissions during acidification and storage

The slurry used in this study was taken from a lagoon of a pig farm located in Rio Maior (Portugal). The liquid fraction (LF) of pig slurry was obtained by sieving (mesh size 100 μm). Half of the screened fraction was preserved at its original pH and the second half was acidified to pH 5.5 by addition of concentrated sulphuric acid. The acidification procedure was as follows: 50 g of liquid fraction were placed into 250 ml plastic containers which were subsequently put into 1.5 l glass jars containing a separate vessel with 20 ml of 1M NaOH solution to trap any CO_2 evolved. Addition of the sulphuric acid to the liquid fraction of slurry was performed using a syringe passed through a septum located in the lid of the jars (see Figure 1). The liquid fraction was stirred during the acidification process. The non acidified liquid fraction was also stirred during the same time period. After 0.25, 0.75, 1.75, 2.75, 3.75, 4.75, 5.75, 29.75, 47.5, 77.5, 149.5 and 197.5 hours, the vessel with 20 ml of a 1M NaOH solution was removed, resealed and stored until analysis for CO_2 and replaced by another vessel with fresh NaOH. The CO_2 trapped in the NaOH was analyzed by a colorimetric method on a segmented flow autoanalyzer (Skalar, The Netherlands, sample flow = 0.16 mL min^{-1}). Each treatment was conducted in triplicate.

2.2 CO_2 emissions after soil incorporation

At the moment of soil incorporation tests, the slurry organic carbon and dry matter content were, respectively, 6.7 g C L^{-1} and 21.3 g.L^{-1} in the acidified slurry, and 5.5 g C L^{-1} and 17.04 g.L^{-1} in the non acidified slurry. Amounts of acidified and non acidified liquid fractions were applied to 60 g of dry soil equivalent at a rate of 0.8 g C kg^{-1} dry

soil. Before the experiment, the soil moisture had been adjusted to 60% of its water holding capacity and then incubated at 25 °C for 7 days in order to slowly re-activate the microbial activity. 250 ml plastic containers containing mixtures of soil+slurry were subsequently put into 1.5 l glass jars containing a vessel with 20 ml of distilled water to avoid soil desiccation and a vessel with 20 ml of 1M NaOH solution to trap any evolved CO_2. A control (soil only) was also used. The jars were sealed with air-tight glass lids and held at 25 °C for 104 days. After 1, 3, 8, 21, 42, 56, 77 and 104 days, the vessel with 20 ml of a 1M NaOH solution was removed, resealed and stored until analysis for CO_2 and replaced by a vessel containing fresh NaOH. The CO_2 trapped in NaOH was analyzed as previously described. Each treatment was replicated 5 times.

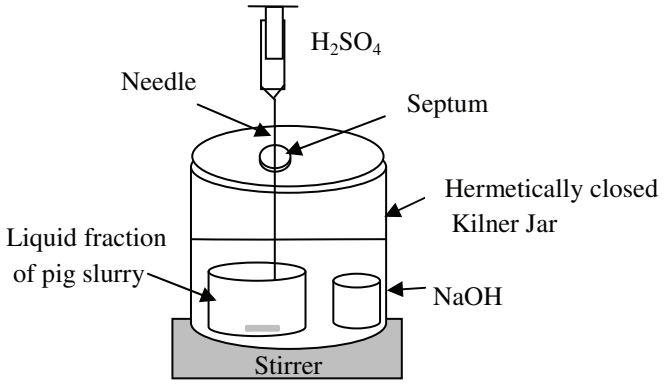

FIGURE 1 **Experimental device used to measure CO_2 emissions during acidification and storage.**

3 RESULTS AND DISCUSSION

3.1 CO_2 emissions during acidification and storage

A strong CO_2 emission was observed immediately after the acidification with about 400 mg C L^{-1} released from the acidified liquid fraction (ALF) compared to only 20 mg C L^{-1} from the non acidified LF during the first 45 minutes of the experiment (Figure 2). However, after 4.75 h, similar CO_2 emissions rates (P<0.05) were observed from the acidified and non acidified liquid fractions after which, CO_2 emissions rates decreased strongly in acidified LF whereas it increased with time in non acidified LF (Table 1). After 60 hours the amount of C released as CO_2 from non acidified LF and acidified LF were very close. Consequently, a higher CO_2 emission was observed from the non acidified LF beyond 30h until the end of the storage trial indicating that most of the CO_2 released early from the acidified LF was released later from the non acidified LF.

TABLE 1 **CO_2 emissions rates (mg C L^{-1} h^{-1}) during storage of acidified and non acidified pi slurry liquid fraction; mean of three replicates**

time (h)	Acidified LF	Non acidified LF
0.25	*719.8[a]	41.7[b]
0.75	447.1[a]	16.1[b]
1.75	62.9[a]	6.9[b]
2.75	9.8[a]	3.2[b]
3.75	8.3[a]	4.3[b]
4.75	9.2[a]	6.4[a]
5.75	7.7[a]	6.5[a]
29.75	2.1[b]	6.5[a]
47.5	2.2[b]	14.5[a]
77.5	1.8[b]	8.9[a]
149.5	0.4[b]	3.5[a]
197.5	0.2[b]	0.9[a]

* Values in a same raw followed by different letters are significantly different (LSD, $P \leq 0.05$).

Vandré and Clemens (1997) also observed enhanced CO_2 emissions after acidification of cattle slurry with HCl (and pronounced foaming) and attributed it mainly to a loss of bicarbonate ions (HCO_3^-).

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$$

The carbon lost as CO_2 during acidification and subsequent storage of acidified LF represents 9% of the total carbon initially present whereas during storage of non acidified LF, the CO_2 released during storage represents more than 15% of the total carbon initially present.

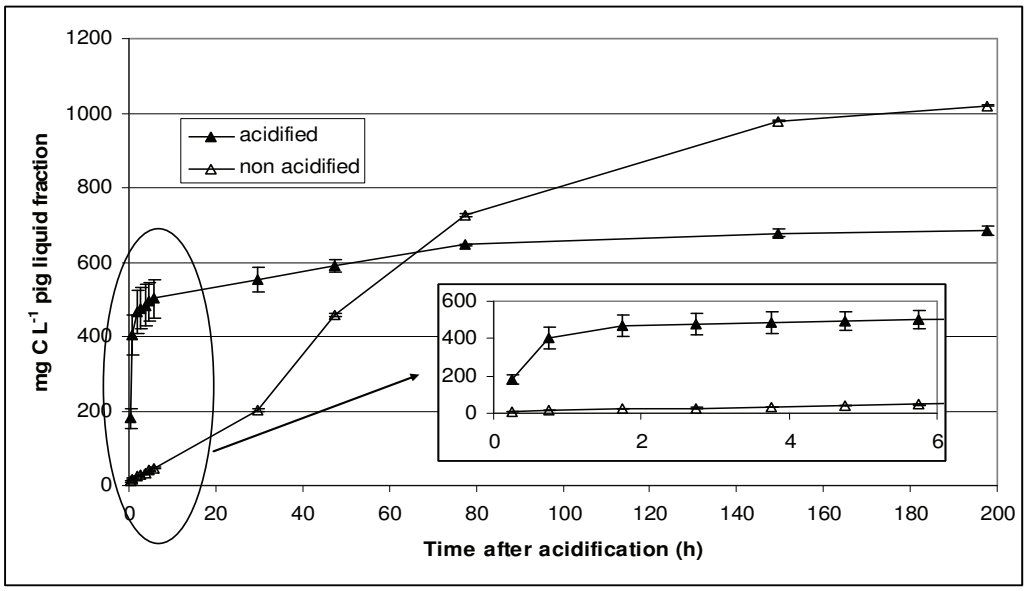

FIGURE 2 **Cumulated amount of C released as CO_2 during storage of acidified and non acidified pig slurry liquid fraction – average and standard error of three replicates. The insert graph shows detail of emissions during the first 6 hours.**

3.2 CO_2 emissions after soil incorporation

The addition of non acidified LF to soil led to a strong increase (more than 900%) of CO_2 emissions relative to the control (soil only) whereas in the case of the acidified LF, such increase was lower than 100% (Figure 3). The differences in terms of CO_2 emissions rates between acidified LF and non acidified LF treated soil diminished after 8 days and reached similar values to the control after 25 days. Several authors (Flessa and Beese, 2000; Fangueiro et al., 2007) attributed such differences to the release of the CO_2 initially dissolved in the LF or produced by transformation of the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions present in the slurry.

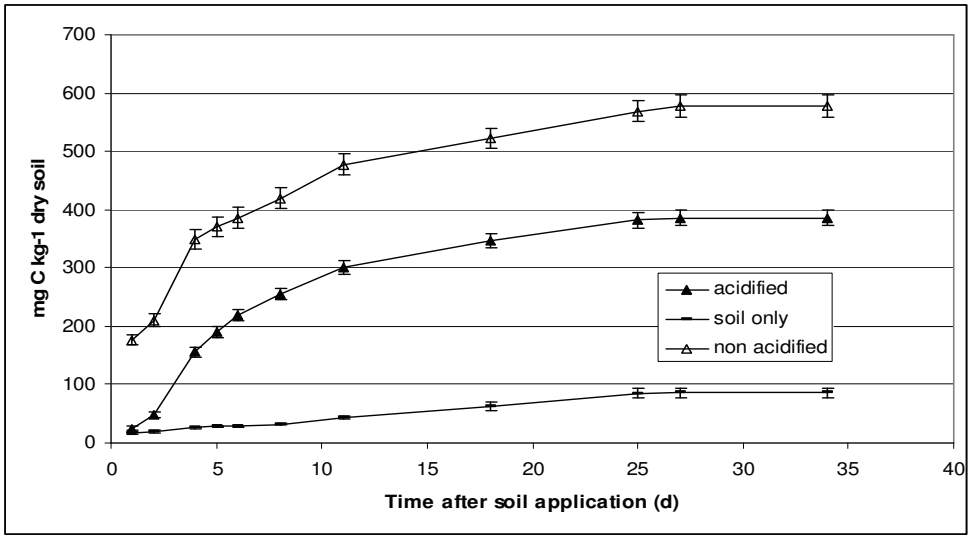

FIGURE 3 **Cumulative amounts of C released as CO_2 from soil mixed with acidified and non acidified pig slurry liquid fraction following storage – average and standard error of five replicates**

For the same reason, CO_2 emissions rates during the first day of the experiment were significantly lower in the acidified LF treatment than in the non acidified LF treatment, since most of the dissolved CO_2 and HCO_3^- /CO_3^{2-} have been lost during the acidification process, prior to soil incorporation. Similarly, Fangueiro et al. (2010) also observed lower CO_2 emissions from soils amended with acidified pig slurry and derived fractions relative to soils amended with non acidified materials. After 34 days of experiment, 72 % of the applied C had been lost as CO_2 in the LF amended soil against only 48% in the ALF amended soil.

4 CONCLUSIONS

In conclusion, LF acidification led to less emissions of CO_2 during slurry storage and following mixing with soil, even if significant CO_2 emissions occurred immediately after acidification. It appears that acidification first removes all the carbonate fraction of the pig slurry liquid fraction but may also have an effect on the microbial activity responsible for organic substrate degradation, explaining the low emissions observed after soil mixing.

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